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SOLID STATE REACTIONS OF CaF_2 WITH OXIDES IN THE PRESENCE OF WATER VAPOR

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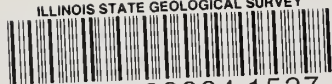
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SOLID STATE REACTIONS OF CaF_2 WITH OXIDES IN THE PRESENCE OF WATER VAPOR

D. L. Deadmore and J. S. Machin

ABSTRACT

This investigation was undertaken to determine the interaction of some common oxides with CaF_2 , with the hope that such information would be helpful in commercial applications in which CaF_2 comes into contact with oxides at elevated temperatures.

It was found that TiO_2 , $\alpha\text{Al}_2\text{O}_3$, α quartz, ZrO_2 , zircon, Fe_2O_3 , and Cr_2O_3 react extensively with CaF_2 when heated to temperatures of 1000 to 1100°C in moist air. MgO , ZnO , and BeO do not react with CaF_2 under these conditions.

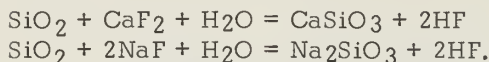
It is suggested that extensive reaction occurs only when compounds or solid solutions are formed between the oxide and CaO .

INTRODUCTION

Calcium fluoride comes into contact with oxides at elevated temperatures in commercial applications such as welding rod coating, glass and enamel manufacture, metallurgical processes, and cement manufacture. The interaction of CaF_2 with the oxides in these complex, multicomponent systems is undoubtedly rather complicated. Therefore, as a first step in gaining a better understanding of these systems, we decided to study the simpler binary systems (actually ternary systems, as water vapor was also present). It is hoped that the information obtained from this study will serve as a guide to the use of CaF_2 in commercial processes and that it may suggest possible new applications of CaF_2 .

Warf et al. (1954) demonstrated that when CaF_2 is heated in contact with U_3O_8 , Al_2O_3 , Cr_2O_3 , or V_2O_5 in the presence of moisture there is considerable interaction. Silverman and Bowen (1959) showed that cryolite in the presence of $\alpha\text{Al}_2\text{O}_3$ is pyrohydrolyzed completely. Powell and Menis (1958) showed that WO_3

and U_3O_8 react with NaF in the presence of moisture. Blau and Silverman (1934) proposed that reactions in fluorine-bearing glasses are of the type:



This report is concerned with the action at elevated temperatures of TiO_2 , $\alpha\text{Al}_2\text{O}_3$, α quartz, ZrO_2 , zircon, Fe_2O_3 , Cr_2O_3 , MgO , ZnO , and BeO on CaF_2 in moist and in dry air.

MATERIALS

All mixtures were prepared by dry mixing the proportioned ingredients with a spatula on a sheet of glazed paper and then shaking them in a bottle. All compositions are expressed in molar terms. Whenever a mole ratio—such as 2:1—is given for a mixture, the first digit refers to the number of moles of oxide and the second to the number of moles of CaF_2 in the mixture.

The TiO_2 used was an industrial grade material that initially was a mixture of rutile and anatase. It was converted entirely to rutile by heating it for several hours at 1000°C before its incorporation into the mixtures. Alpha Al_2O_3 was prepared by calcining aluminum hydroxide at 1350°C for several hours. Silica was finely ground alpha quartz (silica flour) of 99.6 percent purity. The diffraction pattern of the ZrO_2 used showed only monoclinic ZrO_2 to be present. Zircon was industrial G-grade from Titanium Alloy Manufacturing Division, National Lead Company. The MgO , ZnO , Cr_2O_3 , Fe_2O_3 , BeO , and CaF_2 were reagent grade materials.

EXPERIMENTAL METHODS

A controlled atmosphere thermogravimetric balance was used to follow the reactions. X-ray powder diffraction patterns of the residues from these runs were used to identify solid reaction products.

Most of the weight loss runs were made on the loose powder mixtures, but for some the material was dry-pressed in a 5/8-inch diameter, unlubricated steel die before the run. Die lubrication was not allowed as it would have interfered with the weight loss run.

The weight loss data were obtained with the thermogravimetric balance arranged as shown in figure 1. It was constructed so that the atmosphere above the sample could be controlled to some extent.

The furnace temperature was controlled with a conventional potentiometer controller and a Pt—Pt 10 percent Rh thermocouple. The temperature was measured

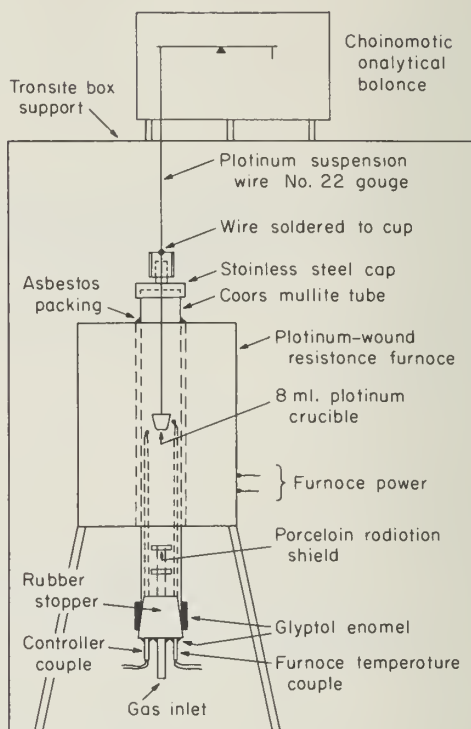
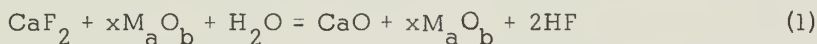


Fig. 1—Thermogravimetric balance used to measure weight loss.

with a manual potentiometer and a furnace temperature thermocouple, also Pt—Pt 10 percent Rh.

Laboratory compressed air, metered with a calibrated capillary tube flow meter and held constant at 0.06 to 0.07 C.F.M., was used as furnace atmosphere in all runs. If dry air was desired, the regulated air stream was passed through two 10-inch drying columns, the first containing anhydrous CaCl_2 , the second anhydrous MgClO_4 . A moist atmosphere was produced by passing the air stream through 200 ml of distilled water contained in a filter flask, the air being dispersed by a fine-pored, sintered glass filter stick. The air-water mixture was passed through a second flask filled with glass wool to trap spray. The temperature of the water was that of the room (26 to 28°C). The air stream was stopped during all weighings to eliminate the unsteady buoyancy effect of the air stream. All runs were made isothermally. The sample was introduced into the furnace, which previously had been brought to the desired temperature, and was weighed periodically.

The initial sample size of the CaF_2 -oxide mixture always was taken so that one gram of CaF_2 was present. The reported weight losses were calculated on the basis of the weight of CaF_2 in the initial sample and not on the total weight of the sample. These values therefore represent the loss in weight of the CaF_2 in the mixture. This method of calculating the weight loss eliminates the influence of varying amounts of oxide in the mixture, as shown below. If the reaction is given by the general equation



where M_aO_b is a metal oxide, there is no change in valence of the oxide cation, and the only volatile component is HF, then complete conversion of the CaF_2 to CaO represents a weight loss of 28.2 percent regardless of the value of x . It will be shown later that there is no appreciable weight loss, thus no appreciable conversion of CaF_2 (under the conditions used here), unless M_aO_b forms a compound or solid solution with CaO. When compounds or solid solutions are formed, the type reaction is better represented by



When $y + z = x$ and there is no volatility (except HF), the weight loss at complete reaction is still 28.2 percent, as it was for reaction (1). The distribution of M_aO_b between y and z depends upon the value of x and the crystallization in the particular system.

All the mixtures show a small, instantaneous weight loss of 2 to 5 percent that must be taken into consideration when the extent of CaF_2 conversion is estimated. This loss probably is due to volatile matter such as water, carbon dioxide from carbonate, and other impurities.

This manner of expressing the weight loss data allows a direct evaluation of the extent of reaction of the CaF_2 with the water vapor and oxide. Therefore, direct comparisons of the reactivity of the various systems can be made when the experimental conditions are alike and the complications discussed above are taken into consideration.

The temperatures of all runs were either 1000 or 1100°C. The choice of these temperatures was based on the fact that CaF_2 when present alone in the moisturized air used in these tests was found to hydrolyze to a negligible extent in periods of up to 24 hours at these temperatures; therefore, any loss greater than

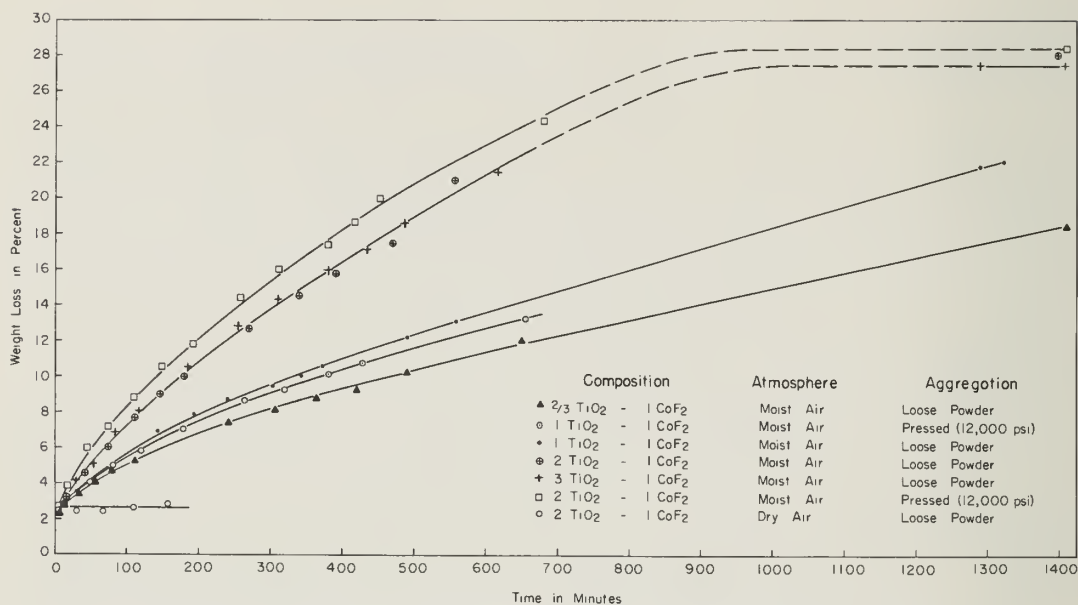


Fig. 2—Weight loss vs. heating time for TiO₂(rutile)-CaF₂ mixtures.
All runs at 1000°C.

the initial, instantaneous loss could be attributed to some interaction of the oxide with the CaF₂. At higher temperatures CaF₂ alone hydrolyzes to a considerable extent (Deadmore, 1960; Bontinck, 1958), which would complicate the interpretation of results. At lower temperatures the oxide-fluoride reactions probably would have been very sluggish.

X-ray powder diffraction patterns of the material remaining after each weight loss run were made using a General Electric XRD-3 diffractometer. Copper K α radiation was used for all compositions except those containing Cr₂O₃ and Fe₂O₃, for which iron K α radiation was used.

EXPERIMENTAL RESULTS

Calcium Fluoride (CaF₂)

Reagent grade CaF₂, when placed in the furnace as a loose powder at 1000°C in moist air, showed an almost instantaneous loss of 2.8 percent, and after 24 hours the loss had increased to 3.8 percent. At 1100°C in moist air the instantaneous loss amounted to 2.6 percent, and after 24 hours the total loss was 5.6 percent.

Titanium Dioxide (TiO₂)

Figure 2 shows the weight loss curves for TiO₂-CaF₂ mixtures. Recalling the fact that CaF₂ when present alone loses only 3.8 percent at 1000°C in moist air over a 24-hour period, it is concluded that losses of 18 to 28 percent over the same period when TiO₂ is present are due mainly to reaction of the TiO₂ with the CaF₂ and water vapor to produce a volatile product, probably HF. As the proportion of TiO₂ in the mixtures increases, the weight loss per unit time also increases until a mixture having a 2:1 ratio is reached, after which a further increase in TiO₂

has no effect. Pressing of the powder into a pellet at 12,000 psi before the run has no uniform influence on the amount lost; the 2:1 mixture shows a slight increase and the 1:1 shows a slight decrease compared to the uncompact material. The amount of weight loss of the 2:1 mixture heated as a loose powder shows a strong dependence on the presence of moisture in the atmosphere. After three hours in dry air there was no noticeable loss beyond the instantaneous loss, but in moist air the loss was considerably greater.

X-ray powder diffraction patterns of all residues from runs made in moist air show CaTiO_3 to be present, but in dry air residues only the starting materials were observed. The 2:1 and 3:1 mixtures, which showed losses of 27 to 28 percent, showed only CaTiO_3 and rutile to be present in their residues. All the CaF_2 had disappeared.

The above information suggests the following reaction:



Aluminum Oxide (Al_2O_3)

The weight loss curves for the $\alpha\text{-Al}_2\text{O}_3\text{-CaF}_2$ mixtures are shown in figure 3. Here again it will be noticed that an increase in the proportion of Al_2O_3 in the mixture increases the weight loss per unit time. Pressing of the samples increased the weight loss for the 2:1 and 5:1 mixtures, but produced no difference for the 1:1 mixture. Raising the temperature 100°C to 1100°C considerably increased the

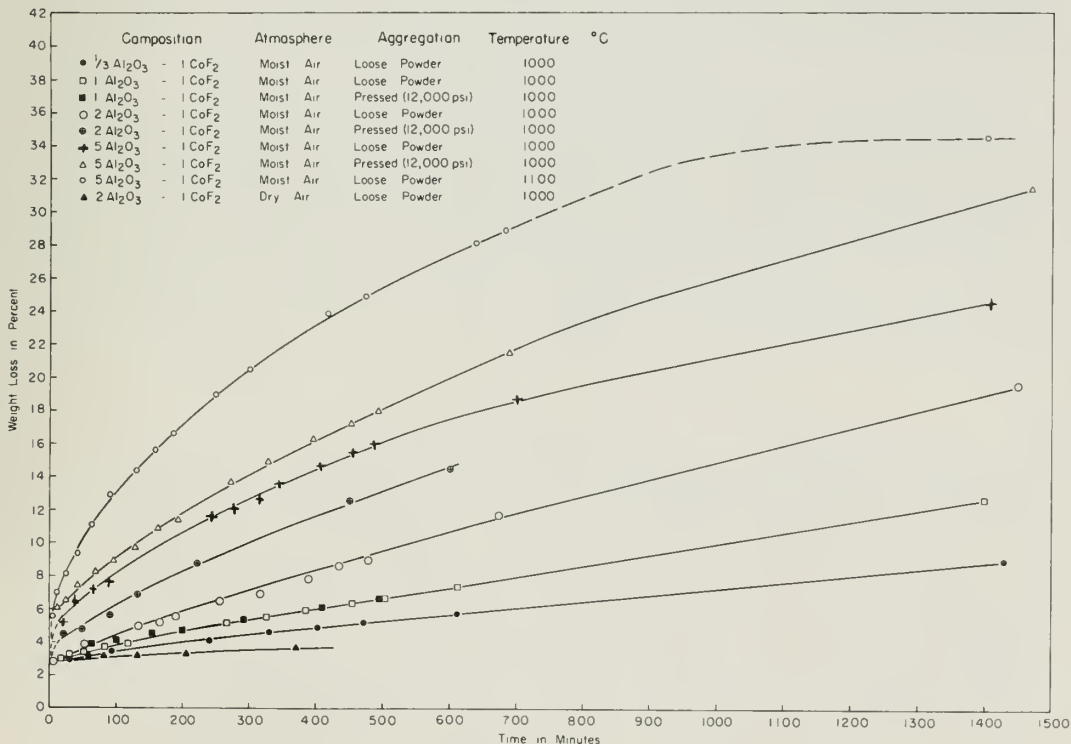


Fig. 3—Weight loss vs. heating time for $\alpha\text{-Al}_2\text{O}_3\text{-CaF}_2$ mixtures.

weight loss of the 5:1 mixture per unit time. The 2:1 mixture when run in dry air shows much less loss than when run in moist air.

Powder diffraction patterns of the 1/3:1, 1:1, and 2:1 mixtures after 24 hours at 1000°C in moist air revealed $\text{CaO} \cdot \text{Al}_2\text{O}_3$ as a new phase, along with CaF_2 and $\alpha\text{Al}_2\text{O}_3$. The presence of CaF_2 indicates incomplete reaction. The 5:1 mixture, after 24 hours at 1000 and 1100°C in moist air as a loose powder, contained $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $\alpha\text{Al}_2\text{O}_3$, and no CaF_2 .

These results indicate that CaF_2 reacts with Al_2O_3 in the presence of moisture to produce calcium aluminates and probably HF.

Silica (SiO_2)

The weight loss data on the 1:1 mixture is given in figure 4. This composition was investigated at 1000 and 1100°C. After 24 hours at 1000°C in moist air as a loose powder, the x-ray diffraction patterns of the residues showed considerable cuspidine ($3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2$) and a small amount of CaF_2 and α quartz. After 25 hours in moist air at 1100°C, much cuspidine was present. After 50 hours at 1100°C (weight loss 29.5 percent), very little cuspidine and no CaF_2 were present. The major component was βCaSiO_3 with smaller amounts of αCaSiO_3 and β and $\gamma\text{Ca}_2\text{SiO}_4$. Brisi (1957) heated a 1/2:1 mixture of CaF_2 and SiO_2 at 900°C in atmospheric air for 300 hours and found cuspidine as the new phase.

From these results it appears that the interaction of CaF_2 and SiO_2 , under the conditions described, first forms cuspidine, which is then converted to calcium silicates, especially at higher temperatures and over extended periods of heating (see Deadmore [1960] and Brisi [1957] on the hydrolysis of cuspidine).

Zirconium Dioxide (ZrO_2)

Figure 5 shows that increasing the proportion of monoclinic ZrO_2 in the mixture increases the weight loss per unit time for the loose powder samples run in moist air. An increase in temperature also greatly increases the weight loss of the 1:1 and 2:1 mixtures. Pressing of the 1:1 and 2:1 mixtures caused no significant change compared to that in the loose powder runs. The 2:1 mixture heated in

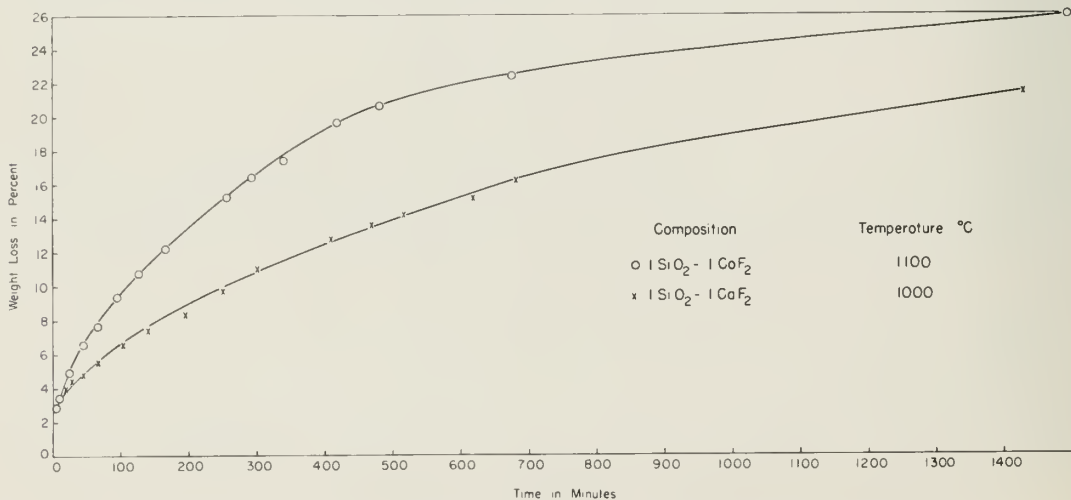


Fig. 4—Weight loss vs. heating time for $\text{SiO}_2\text{-CaF}_2$ mixtures. All samples heated as loose powder in moist atmosphere.

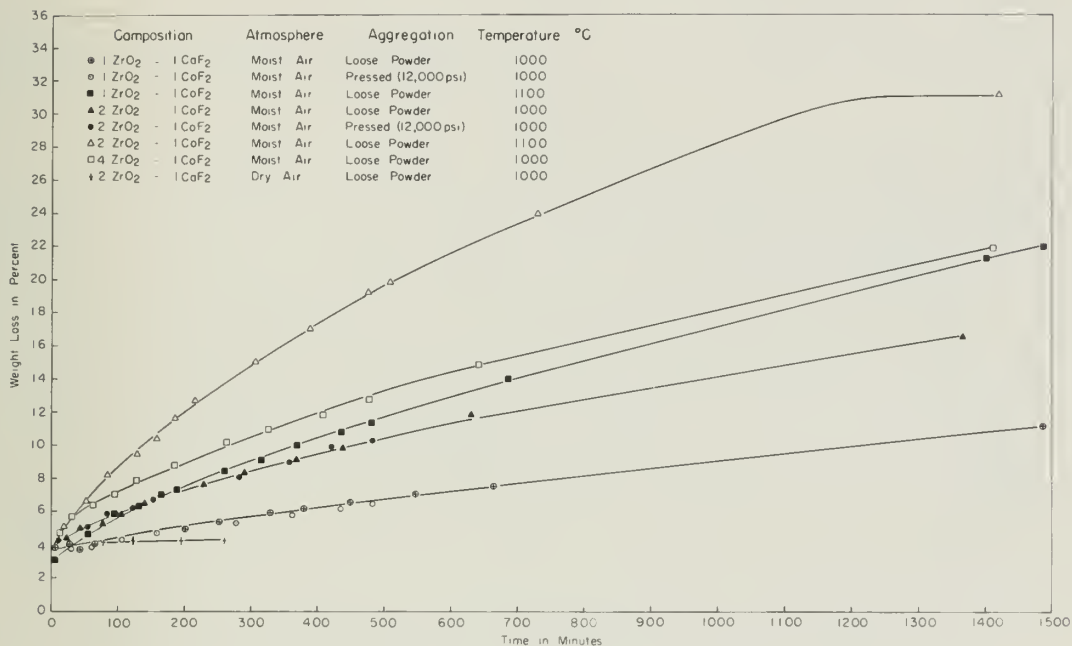


Fig. 5—Weight loss vs. heating time for ZrO_2 - CaF_2 mixtures.

dry air as a loose powder showed about the same amount of instantaneous loss as the run made in moist air, but after four hours of heating in dry air very little further loss was observed.

Diffraction patterns of the 1:1 mixture after 24 hours at 1000 and 1100°C revealed large amounts of CaZrO_3 , along with smaller amounts of CaF_2 and monoclinic and cubic ZrO_2 . The 2:1 mixture after 24 hours at 1100°C contained a large amount of CaZrO_3 and cubic ZrO_2 but no CaF_2 or monoclinic ZrO_2 . After 24 hours at 1000°C the 4:1 mixture contained little CaZrO_3 but large amounts of cubic ZrO_2 and CaF_2 with a moderate amount of monoclinic ZrO_2 .

The reaction of CaF_2 with ZrO_2 in moist air produces the compound CaZrO_3 and cubic ZrO_2 . This cubic ZrO_2 is a solid solution of CaO in ZrO_2 (Duwez et al., 1952).

Zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$)

Figure 6 shows that the addition of zircon to CaF_2 causes the latter to lose weight when heated and that the more zircon in the mixture the greater the loss. Temperature strongly influences the amount of loss per unit time, the $\frac{1}{2}$:1 mixture losing approximately twice as much at 1100° as at 1000°C after 24 hours.

Diffraction patterns of the $\frac{1}{2}$:1 mixture after 24 hours at 1000°C revealed a small amount of cuspidine, large amounts of cubic ZrO_2 , zircon, and CaF_2 , and no CaZrO_3 or monoclinic ZrO_2 . However, after 24 hours at 1100°C an increased amount of cuspidine and a large amount of CaZrO_3 were present, with a smaller amount of cubic ZrO_2 , very little zircon or CaF_2 , and no monoclinic ZrO_2 . Both the 1:1 and 3:1 mixtures after 24 hours at 1100°C contained very little CaF_2 ; about equal amounts of cuspidine, cubic and monoclinic ZrO_2 , and CaZrO_3 were noted along with large amounts of zircon.

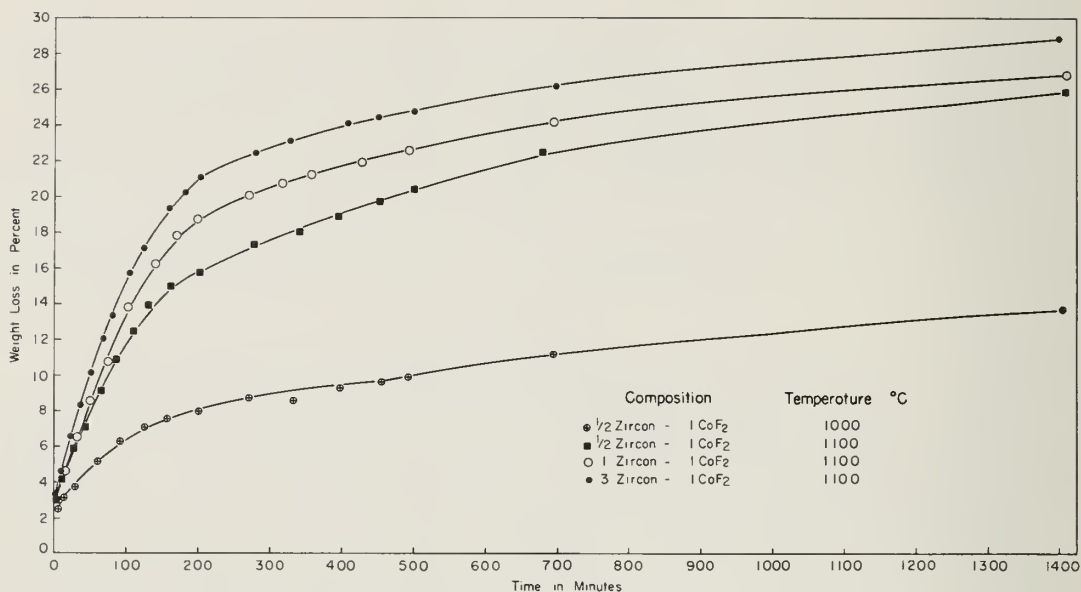


Fig. 6—Weight loss vs. heating time for Zircon- CaF_2 mixtures. All samples heated as loose powders in moist atmosphere.

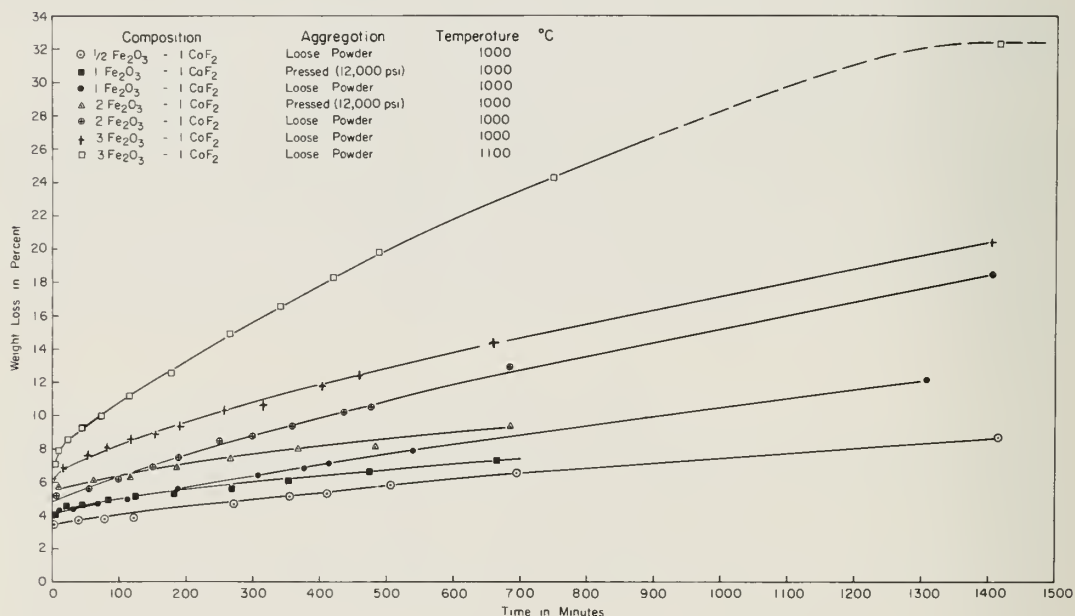


Fig. 7—Weight loss vs. heating time for $\alpha\text{Fe}_2\text{O}_3$ - CaF_2 mixtures. All samples heated in moist atmosphere.

The interaction of zircon with CaF_2 is quite complex, forming as stable products ZrO_2 , CaZrO_3 , and cuspidine.

Ferric Oxide (Fe_2O_3)

Figure 7 shows the weight loss curves for $\alpha\text{Fe}_2\text{O}_3$ - CaF_2 mixtures. The amount of instantaneous loss increases from 3.5 to 6 percent as the proportion of Fe_2O_3 in the mixtures increases. This may indicate that the iron oxide contains some volatile material. If each of the curves is corrected to the initial weight loss of the $\frac{1}{2}$:1 mixture, there is some evidence of an increasing influence of Fe_2O_3 on the weight loss of CaF_2 as the proportion of Fe_2O_3 in the mixture rises. Increasing the temperature from 1000 to 1100°C sharply increases the amount of weight loss for the 3:1 mixture. Pressing the 2:1 and 1:1 mixtures decreases the weight loss noticeably. A run on the 1:1 mixture made in dry air (not shown) exhibited no loss in excess of the instantaneous loss.

Diffraction patterns after 24 hours at 1000°C showed a steady increase in the amount of CaFe_2O_4 and a decrease in CaF_2 as the ratio of $\alpha\text{Fe}_2\text{O}_3$ to CaF_2 increased from $\frac{1}{2}$:1 to 3:1. After 24 hours at 1100°C the 3:1 mixture contained only CaFe_2O_4 , no CaF_2 .

These data suggest that the reaction of Fe_2O_3 and CaF_2 in moist air may be represented by

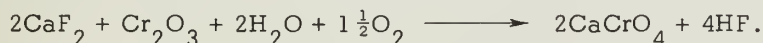


Chromic Oxide (Cr_2O_3)

Two mixtures (1:1 and 3:1 ratios) were heated in moist air as loose powder at 1000°C. Both mixtures exhibited initial losses of 6 to 7 percent, after which they slowly gained 1 to 2 percent during a 24-hour period.

Diffraction patterns of both residues indicated the presence of only CaCrO_4 and Cr_2O_3 . All of the CaF_2 had disappeared.

The weight gain probably is due to oxidation of the Cr^{+3} to Cr^{+6} , as can be seen from a calculation of the weight change for the following reaction:



The calculated weight gain for this reaction is 0.9 percent. The Cr_2O_3 observed to be present in the residues is excess Cr_2O_3 .

Magnesium Oxide (MgO), Zinc Oxide (ZnO), and Beryllium Oxide (BeO)

Only the 1:1 mixtures of each of these oxides were studied. They were heated as loose powders at 1000°C in moist air for periods of 24 hours. It was found that in no case was there any weight loss in excess of the instantaneous loss. Diffraction patterns after cooling showed no new phases to be present in any mixture, so it was concluded that these oxides did not react with CaF_2 under the conditions used here.

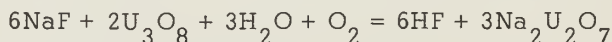
DISCUSSION

Figure 8 summarizes graphically some of the above experimental data. The vertical axis is a plot of the weight loss data after 1000 minutes of exposure of loose powder mixtures to moist air at 1000°C ; the values were taken from the weight loss curves previously given. The time interval was arbitrarily chosen. The vertical scale value at a mole ratio of zero is the weight loss of CaF_2 alone after 1000 minutes under the conditions described.

As the larger values on the vertical scale represent a greater amount of reaction, it is obvious that of all the oxides TiO_2 reacts to the greatest extent per unit time at all mole ratios studied. Fe_2O_3 , Al_2O_3 , and ZrO_2 are much less reactive, and all three appear to be approximately equal in reactivity. MgO , ZnO , and BeO do not react at all at a mole ratio of 1:1.

The question that now arises is why some oxides react extensively with CaF_2 whereas others do not. When the phase diagrams of the added oxide and CaO were examined, it was found that all simple oxides that react form one or more compounds or solid solutions with CaO . Of the nonreacting oxides, only the MgO - CaO diagram was located in the literature and it shows no compound formation. Previous unpublished work carried out in this laboratory on the ZnO - CaO and BeO - CaO systems at temperatures up to 1500°C showed no compound formation or solid solution in either system whether the mixtures were quenched or slowly cooled to room temperature. These facts suggest that there must be compound or solid solution formation between the oxide and CaO if the added oxide is to be reactive toward CaF_2 under the conditions used here.

Warf et al. (1954) have shown that Al_2O_3 , Cr_2O_3 , V_2O_5 , and U_3O_8 react with CaF_2 and NaF while ZnO does not; this agrees with our results. In the case of NaF and U_3O_8 , Warf et al. showed that the reaction is



or a compound is formed.

It was thought that by pressing the loose powder a more intimate contact between the oxide and CaF_2 would result and upon heating a greater loss per unit time might result. The influence of pressing was very erratic. In some cases an increased loss was observed, in others no difference was noted between the loose powder and the compact, and in still others compaction actually decreased the loss. These results suggest that the porosity of the compact, which is controlled by the particle size distribution and packing, are of great importance because water vapor must penetrate to the reaction interface. If porosity is truly the controlling factor, an increase in loss should be noticed in cases where compaction produces a more intimate contact without too large a sacrifice in porosity.

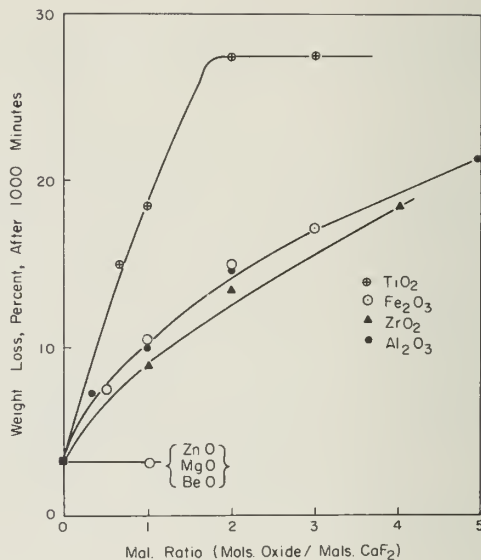


Fig. 8—Weight loss after heating for 1000 minutes vs. the number of moles of oxide per mole of CaF_2 .

In the cases where the porosity is greatly decreased, the loss should be less than that of the loose powders or the increase in intimacy of contact is more than offset by the decrease in porosity.

CONCLUSIONS

TiO_2 , Al_2O_3 , ZrO_2 , Fe_2O_3 , Cr_2O_3 , SiO_2 , and zircon, in the presence of moisture, react with CaF_2 whereas MgO , ZnO , and BeO do not.

In the absence of water vapor, TiO_2 , Al_2O_3 , ZrO_2 , and Fe_2O_3 do not react with CaF_2 .

For those oxides that react it was observed that as the mole ratio of oxide to CaF_2 increased the amount of reaction per unit time also increased.

Compaction produces an erratic effect. In some mixtures it increased weight loss, in others it showed no effect, and in still others it decreased the loss.

An increase in temperature sharply increases the amount of reaction for the oxides that are reactive.

Present evidence suggests that the oxides that react with CaF_2 in moist air form compounds or solid solutions with CaO and that nonreactive oxides do not.

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